AD-A107 646 MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF MATERIA--ETC F/G 20/2
PREPARATION OF INP BY SOLUTION AND MELT GROWTH TECHNIQUES.(U)
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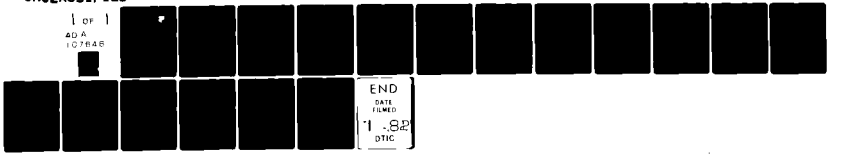

LEVEL II

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RADC-TR-81-231
Final Technical Report
September 1981

PREPARATION OF InP BY SOLUTION AND MELT GROWTH TECHNIQUES

Massachusetts Institute of Technology

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AD

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER RADC-TR-81-231	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) PREPARATION OF InP BY SOLUTION AND MELT GROWTH TECHNIQUES		5. TYPE OF REPORT & PERIOD COVERED Final Technical Report 1 Nov 78 - 30 Nov 80
		6. PERFORMING ORG. REPORT NUMBER N/A
7. AUTHOR(s) August F. Witt		8. CONTRACT OR GRANT NUMBER(s) F19628-79-C-0042
9. PERFORMING ORGANIZATION NAME AND ADDRESS Massachusetts Institute of Technology Department of Materials Science & Engineering Cambridge MA 02139		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62702F 46001734
11. CONTROLLING OFFICE NAME AND ADDRESS Deputy for Electronic Technology (RADC/ESM) Hancom AFB MA 01731		12. REPORT DATE September 1981
		13. NUMBER OF PAGES 18
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) Same		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Same

18. SUPPLEMENTARY NOTES

RADC Project Engineer: John K. Kennedy (RADC/ESM)

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

crystal growth, InP, liquid encapsulation growth, compound semiconductor synthesis

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A modified InP synthesis system has been designed, constructed and put into operation. Basic studies on InP growth have been initiated and deficiencies inherent to the growth system identified. The nature of the effects of liquid encapsulation has been studied using Ga-doped Ge as a model system.

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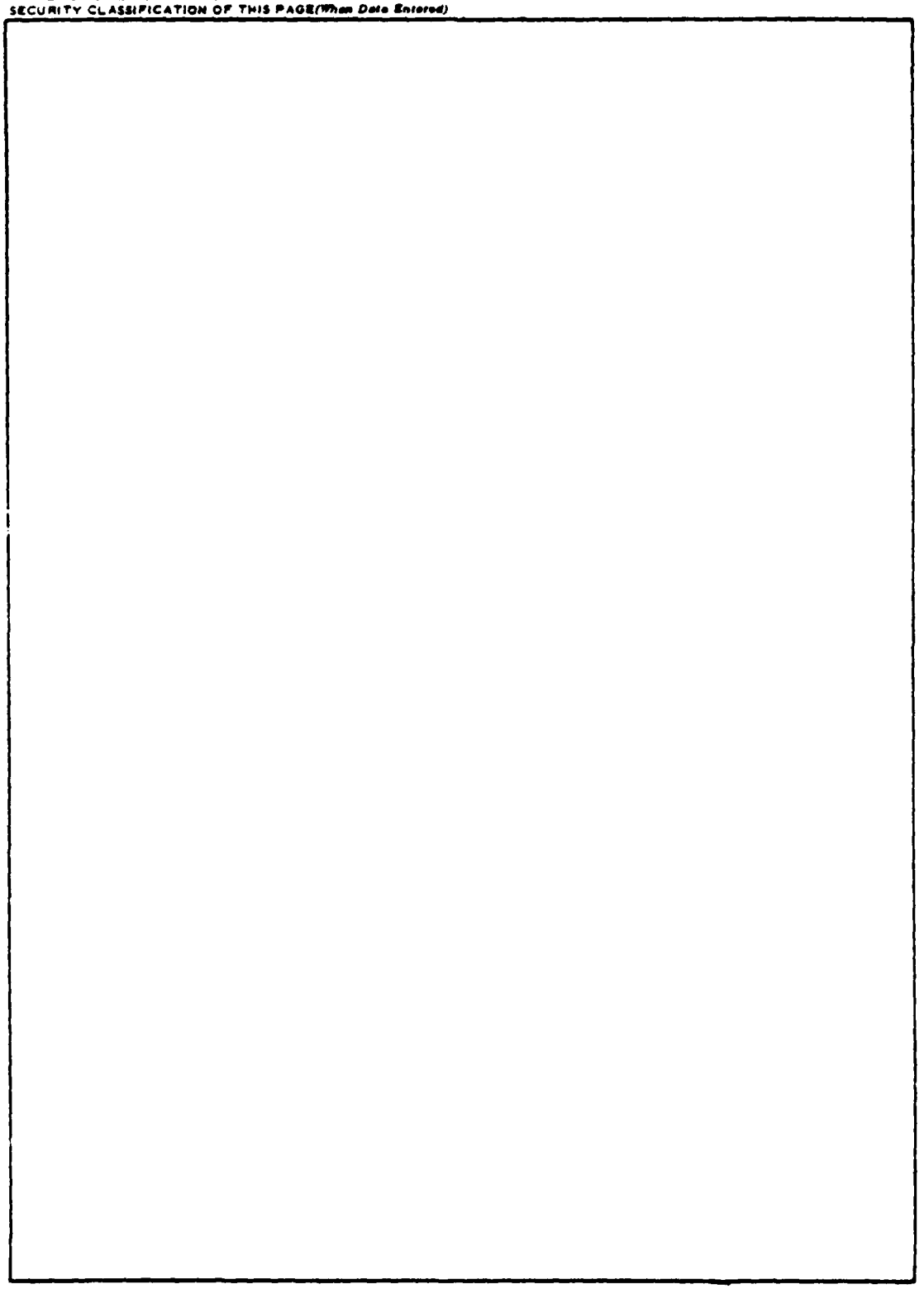


Final Report On

PREPARATION OF InP BY SOLUTION AND MELT GROWTH TECHNIQUES

A. SUMMARY

The thrust of this research was directed at establishing within the Hanscom Air Force Base a capability of synthesizing InP from the constituents and of growing by high pressure LEC single crystals of a degree of chemical and crystalline perfection considered as adequate for device application. The Hanscom Air Force Base was selected for this research (rather than MIT) since the required safety measures could thus more readily be met and at lower expense.

For synthesis of InP, two separate systems were designed and constructed. One system consisted of multi-zone furnaces to establish a temperature spike in the In solution zone ahead of the growth front. The second system operated with coaxial sodium-filled heat pipes for control of the temperature distribution in the high temperature indium solution zone and the low temperature red phosphorus zone.

Analyses of synthesized InP indicate that the best electrical properties can be achieved in ingots if the In solution temperatures are kept low. The results thus obtained are comparable with those reported by industry.

In on-campus research, attention was given to the surface preparation of InP wafers and to the development of etching solutions capable of revealing compositional dopant inhomogeneities in grown single crystals. This research phase was considered a necessary preliminary step for efforts aimed at characterizing and ultimately optimizing liquid encapsulated Czochralski growth in a high pressure pulling system. An ADL growth system was subsequently tested for performance characteristics and modifications were made.

A research program was initiated at MIT directed at determining the effects of liquid encapsulation by B_2O_3 on the thermal convective melt behavior and on basic growth and segregation characteristics. To permit thermal measurements and crystal melt interface demarcation, a model system (Ge-Ga) was selected. It was found that liquid encapsulation during Czochralski pulling has adverse effects on both growth and segregation. Means for optimizing growth conditions are currently under investigation.

B. STAFF ASSOCIATED WITH THIS RESEARCH PROGRAM

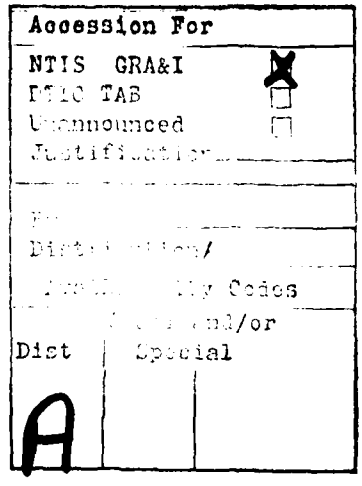
Principle Investigator: A. F. Witt

Research Associate: E. P. Martin

Research Assistant: D. E. Pope

Undergraduate Students: L. Linde
P. Cullen

Engineering Assistant: C. J. Herman



C. RESEARCH REPORT

A two zone synthesis furnace had been designed and assembled. Heat pipes were used to control the temperature distribution of the high temperature indium solution zone and the low temperature red phosphorus zone. The capability for measuring the furnace temperature profile both prior to and during InP synthesis with platinel II thermocouples had been established and the temperature distribution and control of the furnace were optimized.

The first runs, with starting indium solution temperatures ranging between 984°C at the first-to-freeze-end of the boat and 1004°C at the last-to-freeze-end of the boat, a red phosphorus temperature of 461°C (6 atm), and a travel rate of 1.2 cm/day, resulted in polycrystalline ingots. Resistivity and Hall measurements at 77°K on samples cut from single crystal grains revealed the material to be n-type with a carrier concentration of $1.8 \times 10^{15}/cm^3$; the mobility was found to be 39,000 cm^2/volt-sec, and the compensation ratio 0.2. In subsequent synthesis experiments, indium solution temperatures between 1042°C and 1063°C and red phosphorus temperature of 460°C (6 atm) were used with a travel rate of 1.2 cm/day.

A summary of synthesis runs performed in this furnace is shown in Table I. The temperatures reported were measured at the start of the run at 0.75" from the end of the quartz ampoule (Pred), at the front (FOB), and at the back of the quartz boat (BOB). The reported mobility (μ_{77}), carrier concentration (n_{77}), and compensation ratio (θ) are the highest values for each run. For all the runs, GE quartz was used for the boat and the ampoule.

It is found that the best material (highest mobility) is achieved at the lowest boat temperature (in run number 1). This result is attributed to decreased silicon incorporation at the lower temperature. Further support for this interpretation of our findings is seen in the data of run number 2

TABLE I

Summary of Synthesis Runs

Run #	°C Pred	°C FOB	°C BOB	cm/day Travel	cm^2/volt-sec μ_{77}	#/cm^3 n_{77}	θ
1	461	984	1004	1.22	39,300	1.8×10^{15}	0.2
2	460	1042	1063	1.21	19,900	6.4×10^{15}	0.2
3	420	1025	1040	1.13	11,500	1.3×10^{16}	0.3
4	462	1044	1068	1.31	9,200	2.0×10^{16}	0.4
5	461	1041	1069	1.35	5,100	6.2×10^{16}	0.4
6	462	987	1004	1.31	35,700	2.5×10^{15}	0.3
7	465	989	1004	1.28	48,200	1.8×10^{15}	0.1
8	463	990	1004	1.17	43,900	2.2×10^{15}	0.1
9	460	---	1011	1.28	39,600	1.7×10^{15}	0.3

(a) During run, BOB increased to 1090 and was returned to 1065.

* *

where, due to problems in the temperature control circuit, the temperature had increased to 1090°C during the run. Characterization of the resulting ingot indicated a mobility minimum corresponding to the high temperature region. The mobility and the carrier concentration increased and decreased respectively toward the end of the ingot. This behavior suggests the presence of an impurity with an effective distribution coefficient greater than unity with silicon.

To overcome or reduce the effect of silicon incorporation during InP synthesis, a different brand of quartz (Amersil) had been used for the fabri-

cation of ampoules and pyrolytic boron nitride for boats. An additional synthesis apparatus had been assembled which includes a temperature spike in the indium solution zone; this spike was introduced to allow the establishment of a high temperature region ahead of the growth interface while maintaining the bulk of the solution at lower temperatures.

Runs performed in this system are summarized in Table II.

* *

TABLE II

Summary of Synthesis Runs in Spike Apparatus

Run #	°C Pred	°C FOB	°C MAX	°C BOB	cm/day Travel	cm/v-sec μ_{77}	#/cm^3 n_{77}	θ
S1	461	1049	1076	978	1.20	3,100	1.71×10^{17}	---
S2	462	1018	1063	980	1.96	23,400	4.80×10^{15}	0.3
S3	461	1021	1060	936	1.91	9,600	2.30×10^{16}	0.3

Pred = temperature 3/4" under phosphorus from end of ampoule
FOB = temperature at front of boat
MAX = temperature at spike
BOB = temperature at rear of boat
μ_{77} = mobility measured at 77°K
n_{77} = carrier concentration at 77°K
θ = compensation ratio

* *

The ampoules for these runs were prepared in several different ways. Ampoule S1 was of all GE quartz construction and employed the procedure of G. Antypas. Ampoule 7 was prepared with an "Amersil" quartz boat and a GE quartz ampoule using a procedure by G. Iseler. The remaining ampoules were prepared with Amersil quartz using a modification of G. Iseler's procedure.

The modifications consisted of reversing the HCl and HNO_3 etching steps of In.

During the vacuum baking step of run S3, a scum was observed on the surface of the molten In after loading the ampoule. It was found that the In surface could be cleaned by raising the temperature of the In melt to about 600°C. This suggests that the surface layer is composed of the sub-oxide of In which sublimes in vacuum over the temperature range 656-700°C.

The quartz ware for the ampoule in run 8 was baked in an evacuated furnace tube (1000°C). During the bake-out, moisture was observed at the cold end of the tube outside the furnace. After this procedure, the quartz ware was observed to be uniformly carburized, presumably due to a reaction between the moisture and a neoprene vacuum seal. Ampoule 8 was prepared with the quartz ware in this carburized state. The quartz ware for all other ampoules was vacuum baked in a separate sealed-off tube; the individual parts were not carburized.

Prior to run 9 the temperature controllers operating the heat pipe apparatus were replaced by Eurotherm equipment with automatic temperature ramping capability. During the heat-up period of run 9, the high temperature controller failed to stop ramping at the seal-point. Heat transport down the ampoule raised the temperature and resulted in an explosion.

An analysis of results reported in Table I shows that all high In solution temperatures resulted in lower mobility material. From these results it is concluded that higher mobility material is obtained from either the use of Amersil quartz ware in place of Ge quartz ware or the use of G. Iseler's preparation procedure instead of that of G. Antypas. It is also interesting to note that the carburized ampoule, 7, results in the second highest mobility material achieved in this study. It is further worthy of

mentioning that the mobility (at 77°C) of most ingots reaches a maximum value between one and two inches of the first-to-freeze end and then falls off gradually toward the last-to-freeze end.

The results of the spike furnace runs were disappointing.

In the on-campus research phase of this study, the primary focus was placed on the optimization of surface preparation for high resolution etching.

Experiments indicated that the customary surface preparation, involving Br-methanol polishing etchants, is unsatisfactory for subsequent high resolution etching studies aimed at revealing microsegregation. Our research led to a chemical-mechanical polishing procedure involving the following steps:

(1) Grinding of crystal specimen with, consecutively, 25 and 5 μm Al_2O_3 powder.

(2) Chemical-mechanical polishing with Nalcoag-1030 on a Rodel 204-PSA-2 polishing pad for 50 minutes. The polishing solution is diluted 1:4 with deionized water and pH adjusted to 1.5. To enhance the polishing action, 2 ml H_2O_2 is added per liter of solution. (The surface finish thus obtained reveals no surface damage by interference contrast microscopy and yields a highly reflective surface finish.)

Microsegregation studies were pursued, making use of the following basic etch solutions:

(1) H_2SO_4, H_2O_2, H_2O

(2) HF, Cr_2O_3, ($AgNO_3$), H_2O

Our studies indicate that the A-B etchant (Abrahams and Buiocchi) is in principle useful for revealing macrosegregation, but that the suggested addition of $AgNO_3$ has no noticeable consequences and that, moreover, a change in the

ratio of Cr_2O_3 to HF has pronounced effects on the resolution of impurity striations.

Apart from research on surface preparation and high resolution etching, a program was initiated at MIT to provide basic information supportive to liquid encapsulation Czochralski growth of InP through a low pressure LEC model system. Our studies indicate that the growth of Ga-doped Ge encapsulated with B_2O_3 can serve as such a model system in which the following aspects can be investigated:

(1) Interface morphology determination, facet formation and microscopic growth rates;

(2) Cross-correlation of convective behavior and macrosegregation in the longitudinal and radial direction.

The approach taken involves a comparative analysis of conventional Czochralski pulling with LEC. The study is aimed at clarifying the effects of the liquid encapsulant on crystal growth and segregation. In the course of preliminary studies, it was found that heat flow control through the growing crystal can be achieved through the installation of a conical IR reflector located coaxially about the growing crystal. A conventional crystal growth system was accordingly modified and thermocouples were installed for thermal field characterization in the melt.

To optimize the information transfer from our experiments to InP growth simultaneously carried out at Hanscom, bi-weekly visits at RADC were organized, the growth procedures adopted at RADC periodically reviewed and, when indicated, modified.

In the first phase of this study the basic growth and segregation behavior of the pulling facility, which operates with a Na-filled heat pipe located

co-axially about the crucible, was established. It was found that (111) facet formation at the interface extended over 90% of the crystal diameter and that both radial and longitudinal segregation effects were < ±1% of the average dopant level (3×10^{18} cm^3). It was also found that the microscopic rate of growth during rotational pulling was constant to within measurement accuracy (±2%).

The effectiveness of the co-axial IR reflector was tested through the determination of the maximum permissible pulling rate which still yielded a constant crystal diameter. Our investigation showed that this R_{max} could be increased from 3.5 inches/hr to 4.8 inches/hr, which constitutes an increase in excess of 35%. It was also observed that the vertical location of the reflector relative to the melt level has a pronounced effect on the diameter of the crystal grown. Lowering of the reflector yielded a diameter increase, while raising the reflector resulted in a decrease of the crystal diameter. This finding suggests that such reflectors can be used for effective diameter control.

Our studies of the growth of Ga-doped Ge indicated further that the reflector affects significantly the interface morphology of the growing crystal. Specifically, it is found that facet formation is reduced to <50% of the diameter which reduces the probability of undesirable surface nucleation and enhances twin-free growth in Ge.

A comprehensive thermal characterization of the melt in growth configuration for conventional, LEC and modified LEC (with an IR reflector installed) growth was conducted and, in parallel, the macrosegregation behavior in the crystals grown examined. The thermal characterization indicates that the presence of an encapsulant (B_2O_3) increases significantly the frequency and amplitude of temperature fluctuations in the melt. The exact origin of the

enhanced melt perturbation is as yet unclear and is the subject of further studies.

Segregation studies based on spreading resistance measurements reveal that the primary effect of encapsulation on macrosegregation consists of severe perturbations of the diffusion boundary layer at the crystal-melt interface.

It is of interest that LEC action affects predominantly segregation associated with facet growth and only to a minor extent the near-equilibrium segregation associated with off-facet growth.

At this time it is planned to continue this investigation by studying the effects of increased atmospheric pressure on growth by conventional Czochralski and LEC. It is anticipated that this portion of our research program will establish the link to high pressure growth of InP and will permit information transfer from our model studies to InP growth.

D. CONCLUDING REMARKS

The research conducted during the two yar period, involving primarily the establishment of basic synthesis and growth procedures for InP, was of a nature which did not yield publishable results of significance. Rather, the research led to the refinement of processing procedures which form the basis for advanced studies on LEC of broad applicability. Related publications are currently in preparation. An additional consequence of this research phase was the establishment of an intensive collaborative effort on growth of InP involving Hanscom Air Force Base, the Lincoln Laboratory and the Department of Materials Science and Engineering at MIT.

E. REPORTS AND PUBLICATIONS

1. Quarterly Report #1, RADC/ES Contract F19628-79-0042, November 1, 1978, to Janaury 31, 1979.

2. Quarterly Report #2, RADC/ES Contract F19628-79-C-0042, February 1, 1979, to April 30, 1979.

3. Quarterly Report #3, RADC/ES Contract F19628-79-C-0042, May 1, 1979, to July 31, 1979.

4. Quarterly Report #4, RADC/ES Contract F19628-79-C-0042, August 1, 1979, to October 31, 1979.

5. Quarterly Report #5, RADC/ES Contract F19628-79-C-0042, November 1, 1979, to January 30, 1980.

6. Quarterly Report #6, RADC/ES Contract F19628-79-C-0042, February 1, 1980, to April 30, 1980.

7. Quarterly Report #7, RADC/ES Contract F19628-79-C-0042, May 1, 1980, to July 30, 1980.

8. Quarterly Report #8, RADC/ES Contract F19628-79-C-0042, August 1, 1980, to October 30, 1980.

9. Q.-M. Zhou and A. F. Witt, "Effects of Liquid Encapsulation on Crystal Growth and Segregation During Czochralski Pulling", accepted for presentation at ICVGE-5/ACCG-5 and in preparation for publication.

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